Silica-Supported $KHSO_4$: An Efficient System for Activation of Aromatic Terminal Olefins

Ram Nath Das, Kuladip Sarma, Madan Gopal Pathak, Amrit Goswami*

Synthetic Organic Chemistry Division, North-East Institute of Science & Technology (A Constituent Establishment of CSIR, New Delhi), Jorhat, Assam 785006, India
Fax +91(376)2370011; E-mail: amritg_2007@rediffmail.com

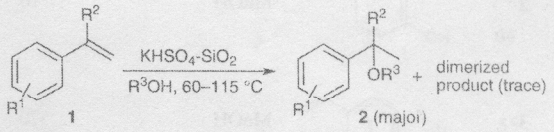
Received 21 July 2010

Abstract: Potassium hydrogen sulfate adsorbed on chromatography-grade silica gel activates electron-rich aromatic terminal olefins towards nucleophilic attack at the benzylic position by alcohols. Temperature plays a crucial role and facilitates suppressing nucleophilic reaction in favor of dimerization of the terminal olefin.

Key words: alkenes, alkoxylation, dimerization, potassium hydrogen sulfate, silica gel

Activation of terminal alkenes is a challenging task in organic chemistry for preparation of industrially important higher alkenes, lubricants and detergents through homo- and co-dimerization.[1] Effective activation of alkenes by transition metals iron,[2] copper,[3] titanium on montmorillonite support,[4] zirconium,[5] ruthenium,[1] rhodium,[6] palladium,[7–9] gold and platinum catalysts,[10] sometimes in the presence of co-catalysts[11] has been reported for formation of C–C or C–heteroatom bonds. Use of proton-exchanged montmorillonite as a solid Brønsted acid has been reported to be another extremely effective catalyst for direct addition of alkenes and alcohols to active methylene of 1,3-dicarbonyl compounds.[12] Direct formation of C–C or C–O bonds by coupling of an alkene with another or with an alcohol through functionalization of the C=C bond at the benzylic position is thus a very attractive reaction. The problem in the use of late transition metals in many processes is their high cost and toxicity. On the other hand, zeolites and other polymeric solid supports suffer from limitations of pore-size dependency and requirement for large quantities. Therefore achieving an alternative perspective on this conversion is definitely highly appealing.

Although triflic acid adsorbed unmodified chromatographic silica has been studied as effective recyclable system for alkylation of β-dicarbonyl compounds with alcohols or olefins,[13] formation of C–C or C–heteroatom bond through activation of alkenes by readily available and cheap alkali metal salts has not been explored. When the surface area of such metal salts is increased by supporting on a solid matrix, it constitutes an attractive heterogenous catalyst system with improved activity and selectivity.



R^1 = H, OH, OMe, OBn, OCOMe
R^2 = H, Me
R^3 = Me, Et, *i*-Pr, Bu,
$C_6H_5(CH_2)_4$, $C_6H_5CH(Me)$

Scheme 1

Thus silica-supported $KHSO_4$ and $NaHSO_4$ have been developed for cleavage of TBDMS ethers[14] and esters,[15] acetal preparation[15] and as dehydrating agents.[16] We have observed a novel property of this system and herein we present our experimental results for activation of aromatic terminal alkenes leading to cross-coupling with alcohols by nucleophilic attack on the benzylic carbon atom and also dimerization (Scheme 1).

Deprotection[17] of 4-acetoxystyrene by silica-supported $KHSO_4$ in methanol at its reflux temperature revealed that the alkenic double bond was attacked by methanol in the benzylic position to yield 1-(4-hydroxyphenyl)-1-methoxyethane in good yield (entry 1, Table 1). The reaction product was accompanied by a trace amount of head-to-tail dimerized product of 4-hydroxystyrene. Gratifyingly similar results were observed with a range of styrenes having electron-releasing group (entries 2–4, Table 1) on the benzene ring. Styrenes having electron-withdrawing groups on the benzene ring such as Cl or NO_2 showed disappointing results.

Intrigued by the unusual mode of this reaction, a systematic investigation of the reaction of styrene derivatives was carried out with a range of higher alcohols in the presence of silica-supported $KHSO_4$ at 80–115 °C (entries 5–9, 13 and 14, Table 1). Depending upon the alcohol, a specific reaction temperature (80–115 °C, Table 1) was required for nucleophilic insertion at the benzylic carbon of the substrate to occur (10–73%) along with the parallel dimerization reaction to give **4** (15–56%, Table 1). In the reaction of 4-methoxystyrene in a toluene–methanol (4:1) solvent system, it was observed that the dimerization reaction predominated over nucleophilic insertion with increase of reaction temperature (Figure 1). The reaction did not proceed with a tertiary alcohol; in the case of a secondary alcohol it was found to be sluggish (entries 7 and 9, Table 1).

SYNLETT 2010, No. 19, pp 2908–2912
Advanced online publication: 10.11.2010
DOI: 10.1055/s-0030-1259041; Art ID: D19910ST

Table 1 Reaction of Different Styrene Derivatives with Different Alcohols using $KHSO_4$–SiO_2 System

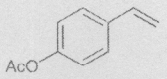
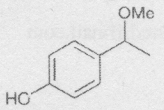
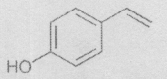
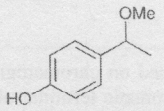
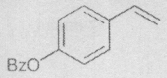
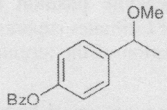
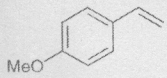
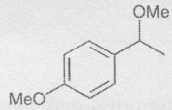
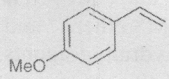
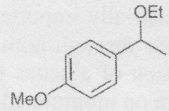
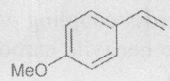
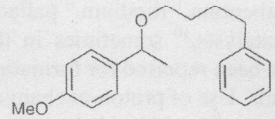
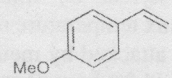
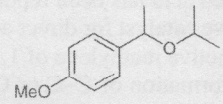
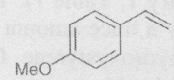
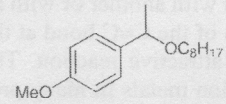
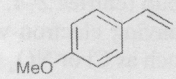
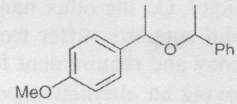
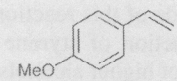
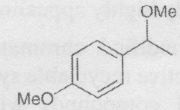
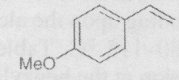
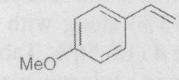
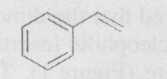
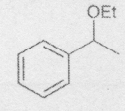
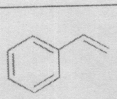
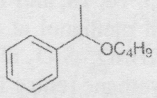
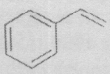
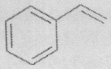
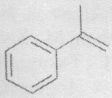
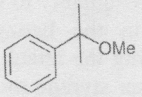
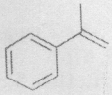
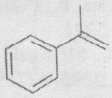
Entries	Substrates	Solvent	Temp (°C)	α-Alkoxylated product[b] (A)	Dimerized product[b] (B)	Time (h)	Yield[c] (%)	
							A	B
1		MeOH	70		N.O.[d]	3	84	–
2		MeOH	70		N.O.[d]	3	87	–
3		MeOH	70		N.O.[d]	3	82	–
4		MeOH	70		4	3	65	30
5		EtOH	80		4	3	20	45
6		4-phenyl-1-butanol	115		4	4	45	50
7		2-PrOH	115		4	5	11	55
8		*n*-octanol	115		4	5	15	56
9		1-phenylethanol	115		4	5	10	35
10		toluene–MeOH (4:1)	115		4	3	25	61
11		DCE	80	–	4	3	–	63
12		toluene	115	–	4	3	–	65
13		EtOH	80		3	3	10	25

Table 1 Reaction of Different Styrene Derivatives with Different Alcohols using $KHSO_4$–SiO_2 System (continued)

Entries	Substrates	Solvent	Temp (°C)	α-Alkoxylated product[b] (A)	Dimerized product[b] (B)	Time (h)	Yield[c] (%) A	Yield[c] (%) B
14		*n*-BuOH	80		3	4	73	15
15		toluene	115	–	3	3	–	66
16		DCE	80	–	3	3	–	64
17		MeOH	70		5	3	26	55
18		toluene	115	–	5	3	–	59
19		DCE	80	–	5	3	–	58

[a] The reactions were run with olefin (8–10 mmol) for 3–6 h.[20]
[b] The products were characterized from their respective IR, NMR, GC and mass spectroscopic data and by comparison with literature data.[21]
[c] Isolated yields of products.
[d] The products were not observed (N.O.).

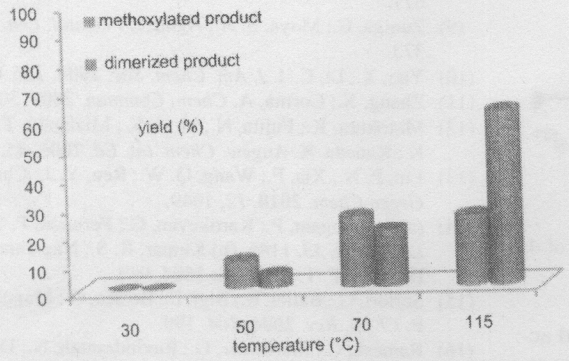
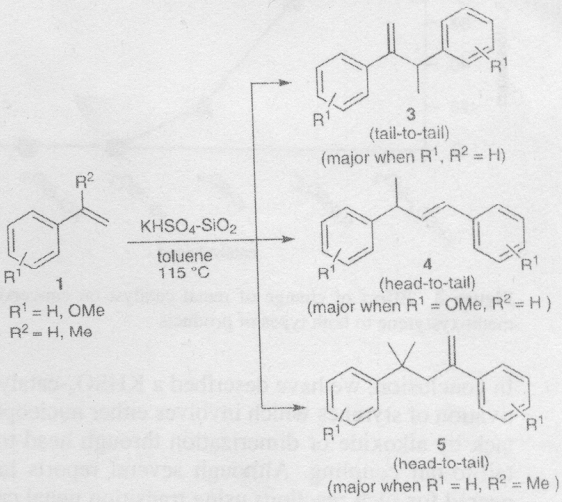


Figure 1 Effect of temperature on dimerization of 4-methoxystyrene in toluene–MeOH (4:1) solvent system



Scheme 2

However, in aprotic solvents like dichloroethane and toluene, dimerization reaction of 4-methoxystyrene occurred exclusively to give 63–65% yield (Scheme 2; entries 10–12, Table 1) of the head-to-tail dimerized product **4** along with a trace amount of another dimerized product. Such a product was reported[18] to be formed from styrene on reaction with trifluoroacetoxy nickel hydride in 40 hours.

Styrene itself did not undergo any reaction when refluxed in methanol in the presence of silica-supported $KHSO_4$. However, when heated in ethanol at its boiling point, styrene gave 1-phenyl diethylether (10%) and tail-to-tail dimerized product **3** (25%) having a terminal double bond (Scheme 2; entry 13, Table 1), which is reported[19] to be formed from styrene on reaction with cyclopalladated tetrafluoroborate from *N*-(*p*-tolyl)-*p*-nitrobenzalidimine at 100 °C over 19 hours. Surprisingly, styrene on refluxing with *n*-butanol in the presence of silica-supported $KHSO_4$ at 80 °C for three hours gave 73% of *n*-butyloxy-1-phe-

nylethanol and only 15% of tail-to-tail dimerized product **3** (Scheme 1; entry 14, Table 1). On the other hand styrene or α-methylstyrene on heating with silica-supported $KHSO_4$ in dichloroethane or in toluene, gave 58–66% yields of tail-to-tail and head-to-tail dimerized products **3** and **5**. respectively (Scheme 2; entries 15, 16, 18, and 19, Table 1). α-Methylstyrene on heating in methanol at its reflux temperature in the presence of $KHSO_4$–SiO_2 also gave 26% of 1-methyl-1-phenylmethoxyethane (entry 17, Table 1) and 55% of head-to-tail dimerized product **5** (Scheme 2). It is postulated that the absence of any electron-releasing group on the benzene ring facilitates tail-to-tail dimerization over head-to-tail dimerization. The role of the electron-releasing substituent in both the nucleophilic addition and the dimerization is presumably to stabilize the carbonium ion generated in the benzylic position by potassium bisulfate facilitating the attack by nucleophilic methoxy group or by another styrene molecule. This is not possible in the case of substrates having electron-withdrawing groups.

The reaction was studied with other sodium and potassium salts such as $NaHSO_4$, K_2SO_4, KCl and KF. However, compared to $KHSO_4$ all other salts showed inferior or no catalytic activity (Figure 2). The detailed assignment of the ^1H NMR spectra of **3–5** and comparison with the literature data established their structures (Scheme 2).

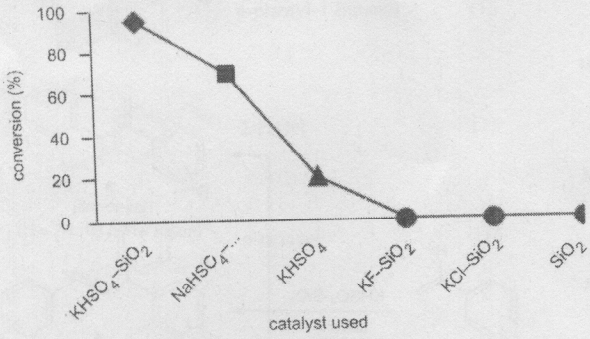


Figure 2 Effect of change of metal catalyst on conversion of 4-methoxystyrene to both types of products

In conclusion, we have described a $KHSO_4$-catalyzed activation of styrenes which involves either nucleophilic attack by alkoxide or dimerization through head-to-tail or tail-to-tail coupling. Although several reports have appeared for such reactions using transition metal catalysts, the solid-supported acidic salt mediated catalyzed reactions described in this communications represent the first report of C–C and C–O functionalization. The advantages of the method are that it is a one-pot process, noncorrosive, the catalyst can be easily recovered for recycling and the procedure is simple.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

We gratefully acknowledge Dr. P. G. Rao, Director, NEIST, Jorhat for providing the facilities to carry out this work. The authors also gratefully acknowledge Dr. J. C. S. Kataky, Head, Synthetic Organic Chemistry Division for his help with carrying out this work and CSIR, India for the funding.

References and Notes

(1) (a) Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 4715. (b) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284. (c) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (d) Aljarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 1. (e) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (f) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (g) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353. (h) Kondo, T.; Takagi, D.; Tsujita, H.; Ura, Y.; Wada, K.; Mitsudo, T.-A. *Angew. Chem. Int. Ed.* **2007**, *46*, 5958.

(2) Zhang, S.-Y.; Tu, Y.-Q.; Fan, C.-A.; Zhang, F.-M.; Shi, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 8761.

(3) (a) Wang, D.; Li, J.; Li, N.; Gao, T.; Hou, S.; Chen, B. *Green Chem.* **2010**, *12*, 45. (b) Zaccheria, F.; Psaro, R.; Ravasio, N. *Tetrahedron Lett.* **2009**, *50*, 5221.

(4) Motokura K., Fujita N., Mori K., Mizugaki T., Ebitani K., Kaneda K.; *J. Am. Chem. Soc.*; **2005**, 127: 9674.

(5) Sultanov R. M., Vasil'ev V. V., Dzhemilev U. M.; *Russ. J. Org. Chem.*; **2010**, 46: 355.

(6) Tobisu M., Hyodo I., Onoe M., Chetani N.; *Chem. Commun.*; **2008**, 6013.

(7) Tsuchimoto, T.; Kamiyama, S.; Negoro, R.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* **2003**, 862.

(8) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677.

(9) Zuniga, C.; Moya, S. A.; Aguirre, P. *Catal. Lett.* **2009**, *130*, 373.

(10) Yao, X.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884.

(11) Zhang, X.; Corma, A. *Chem. Commun.* **2007**, 3080.

(12) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 2605.

(13) Liu, P. N.; Xia, F.; Wang, Q. W.; Ren, Y. J.; Chen, J. Q. *Green Chem.* **2010**, *12*, 1049.

(14) (a) Arumugam, P.; Kartikeyan, G.; Perumal, P. T. *Chem. Lett.* **2004**, *33*, 1146. (b) Kumar, R. S.; Nagarajan, R.; Perumal, P. T. *Synthesis* **2004**, 949.

(15) Sartori, G.; Balini, R.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. *Chem. Rev.* **2004**, *104*, 199.

(16) Ramesh, C.; Mahender, G.; Ravindranath, N.; Das, B. *Tetrahedron Lett.* **2003**, *44*, 1465.

(17) Goswami, A.; Das, R. N.; Borthakur, N. *Indian J. Chem., Sect. B* **2007**, *46*, 1893.

(18) Dawans, F. *Tetrahedron Lett.* **1971**, 1943.

(19) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238.

(20) (a) **Catalyst Preparation**: $KHSO_4$ (20 g, 144 mmol) was dissolved in distilled H_2O (100 mL) and silica gel (25 g, 60–120 mesh) was added. The soaked mixture was thoroughly mixed and dried in a hot oven at 150 °C for 24 h to give a free flowing powdery solid. The dried solid mixture was then stored in a vacuum desiccator. (b) **Typical Experimental Procedure for Alkoxylation**: 4-Methoxystyrene (1 g, 7.5 mmol) was added slowly to a round-bottomed flask containing $KHSO_4$–SiO_2 (100 mg) and 4-phenyl-1-butanol (5 mL). The mixture was then stirred

for 3 h at 115 °C to give 1-(4-methoxyphenyl)-1-(4-phenyl-1-butoxy)ethane (0.96 g, 45%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$; Me_4Si): δ = 1.33 (d, *J* = 6.4 Hz, 3 H, CH_3CHOCH_2), 1.58 (m, 4 H, $PhCH_2CH_2$), 2.51 (m, 2 H, $OCH_2CH_2CH_2$), 3.20 (t, *J* = 6.4 Hz, 2 H, OCH_2CH_2), 3.73 (s, 3 H, $PhOCH_3$), 4.24 (q, *J* = 6.4 Hz, 1 H, CH_2OCHCH_3), 6.80 (d, *J* = 6.8 Hz, 2 H, 2 × MeOAr-*m*-*H*), 7.06–7.21 (m, 7 H, 7 × Ar*H*). ^{13}C NMR (75 MHz, $CDCl_3$; Me_4Si): δ = 24.2 (CH_3CHOCH_2), 28.1, 29.6, 35.8, 55.3 (4 × CH_2), 68.3 (CH_3CHOCH_2), 113.8 (OCH_3), 125.7, 127.4, 128.3, 128.5, 136.2, 142.6, 158.9 (12 × Ar*C*). MS: *m*/*z* (EI) = 284 [M$^+$]. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.28; H, 8.45. Found: C, 80.32; H, 8.41. (c) **Typical Procedure for Dimerization**: A solution of 4-methoxystyrene (1 g, 7.5 mmol) in toluene (2 mL) was added slowly to a round-bottomed flask containing $KHSO_4$–SiO_2 (100 mg) in toluene (10 mL). The mixture was then stirred for 3 h at 115 °C to give the head-to-tail dimmer, 1,3-di-(4-methoxyphenyl)-1-butene (0.65 g, 65%) as a semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$; Me_4Si): δ = 1.40 (d, *J* = 6.5 Hz, 3 H, CH_3CH), 3.56 (q, *J* = 6.5 Hz, 1 H, CH_3CHCH), 3.79 (s, 6 H, 2 × $PhOCH_3$), 6.23–6.36 (m, 2 H, CH=CH), 6.80–6.87 (m, 4 H, 4 × ArH), 7.17–7.29 (m, 4 H, 4 × ArH). ^{13}C NMR (75 MHz, $CDCl_3$; Me_4Si): δ = 21.5 (CH_3CH), 41.7 (CH_3CH), 55.3 (2 × OCH_3), 113.9 (2 × Ar*C*), 127.3, 127.6 (2 × CH=CH), 127.8, 128.2, 128.4, 129.9, 130.5, 133.5, 138.0, 157.9, 158.8 (10 × Ar*C*). MS: *m*/*z* = (EI) 268 [M$^+$]. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.59; H, 7.46. Found: C, 80.54; H, 7.49.

(21) (a) Fujii, Y.; Furugaki, H.; Tamura, E.; Yano, S.; Kita, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 456. (b) Zaccheria, F.; Psaro, R.; Ravasio, N. *Tetrahedron Lett.* **2009**, *50*, 5221. (c) Murphy, J. A.; Khan, T. A.; Zhou, S.; Thomson, D. W.; Mahesh, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1356. (d) Zhang, Y.; Sigman, M. S. *Org. Lett.* **2006**, *8*, 5557. (e) Minai, M.; Higashii, T. Eur. Patent Appl. EP 288297, **1988**.